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Glutinous Water

Protecting Vertical and Overhead Surfaces From Fire Spread

HOMER W. CARHART

*Navy Technology Center for Safety and Survivability
Chemistry Division*

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13. ABSTRACT (Maximum 200 words) Most of the water used in firefighting is not only wasted, it also contributes extensively to total damage. Water is an unusual chemical in that, due to hydrogen bonding, it is a liquid at room temperature and it also has a very high heat of evaporation. So, if one could make water adhere significantly to vertical and overhead surfaces, a great deal of fire protection could be "bought" because such surfaces could not get hotter than the boiling point of water (100°C) and a great deal of heat energy would be required to evaporate it. This can be accomplished by making water <u>glutinous</u> , either by making a foam (e.g., shaving cream) or by thickening it (e.g. gravy), or both. Calculations and experiment show that up to at least 10 times greater fire protection could be achieved with only about 1/20 - 1/50 the amount of water.			
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GLUTINOUS WATER

PROTECTING VERTICAL AND OVERHEAD SURFACES FROM FIRE SPREAD

PROLOGUE

One need not argue that the substance called "water" is a fabulous firefighting agent. Were it not so ubiquitous, the chemical manufacturing industry would be "busting a seam" to make it, and sell it at a handsome price, for that very purpose. But, are we taking full advantage of its unusual properties? Perhaps we don't because it is too ubiquitous, too available. We therefore tend to "drown" a fire, with concomitant extensive water damage, sometimes estimated to be as high as 60-70% of the total "fire damage". In the maritime world one has only to recall the vaunted French luxury liner "Normandie" which from the weight of excessive firefighting water turned over on its side and came to rest on the mud at its pier in New York in 1942. In the Persian Gulf in 1987 the USS STARK was set on fire by hits from 2 missiles and developed a 15° list from undrained firefighting water seriously hampering the firefighting itself.

Fundamentally, in today's firefighting practices, a guesstimate is that we waste well over 90% of the water "thrown" at a fire, which then finds itself free to do mischief and damage in addition to that of the fire. Even the remaining 10% (or less) is not used to maximum effectiveness, which, if it were, would also markedly reduce the total damage not only by water but also by minimizing the spread of the fire itself.

Fire Behavior

Fires propagate in sort of a boot-strap operation. For Class B (liquid fuel) fires, heat energy is needed in a feed-back manner to evaporate the fuel so it can burn. For Class A (solid fuel) fires, energy is needed to heat unburned material ahead of the flame front to its "kindling" temperature to propagate the fire. This heat energy is transferred from a fire by both convection (hot gas) and radiation (largely infra-red). But, as the fire gases and entrapped air are heated in a fire, they expand and become less dense, and because of gravity, become buoyant and rise, and then, whether they transfer energy back to the fire depends very much on the geometry or spatial arrangement of the fuel, i.e., if the unburned fuel is above the fire, then the hot gases are very important in energy transfer, otherwise most of this energy is

dissipated to the atmosphere. On the other hand, radiant energy is transferred by line of sight in all directions, up, down or sideways equally, so in many instances it can become more important in the energy transfer process.

For common liquid fuels (Class B fires) to burn, the liquid must first evaporate and mix with air. (Contrary to an all-too-common belief, such fuels do not burn in the liquid phase even when sprayed or atomized). The rising burned (hot) gases do little to heat the liquid to help evaporate it. Thus, most of the feed-back heat energy needed to do so is by radiation from the luminous flame back to the surface.

Class A fires are a different matter. For many solids, we can think of burning as existing in 2 modes - flaming and smoldering. Their mechanisms are different. In flaming combustion, what happens is that both radiant and convective heat energy from the fire pyrolyzes unburned material ahead of the flame front to generate combustible gases which then mix with air and burn. This added energy contributes to the increasing growth of the fire. Heating by radiation is very important to the phenomenon called "flash-over", wherein the amount of combustible gases generated become so high that on ignition they become almost explosive. As with a liquid pool fire, flaming combustion in a Class A fire can also be thought of as being dependent on surfaces, not volumes, because it is the surface that gets heated first, and that is where pyrolysis starts. This concept is important to the discussion that follows. .

A smoldering (deep-seated) fire usually follows a flaming fire, and takes longer to get established. Much of it results from direct air oxidation in the structure of the charred material. In most unwanted Class A fires, smoldering contributes a much smaller portion to fire propagation and growth than flaming combustion. So, it is the latter we need concern ourselves with here.

The Unusual Qualities of Water

To begin with, if one considers its molecular weight and the properties of hydrides of the lighter elements close to oxygen in the Periodic Chart, it would appear that water should be a gas rather than a liquid at room temperature. Table I shows the boiling points of these hydrides.(1)

Table 1 - Boiling Points of Hydrides of Lighter Elements

Name	Methane	Ammonia	Water	Hydrogen Sulfide
Formula	CH ₄	NH ₃	H ₂ O	H ₂ S
Molecular Wt.	16	17	18	34
Boiling Pt. (°C)	-162	-33	+100	-60

In the Periodic Chart, sulfur is directly below oxygen (Group VIA), and, therefore, its compounds and derivatives might be expected to exhibit properties similar to the corresponding oxygen compounds. But its hydride (H_2S) has a boiling point of $-60^\circ C$ (compared to water (H_2O) at $+100^\circ C$) and thus is a gas at ordinary temperatures.

The explanation given as to why water is a liquid at room temperature is based on the phenomenon called hydrogen bonding. This denotes the ability of a hydrogen atom on one water molecule to develop a significant intermolecular attachment to the oxygen of an adjacent water molecule. This gives the water molecules a propensity to stick to each other to form clusters thereby markedly increasing their effective size and molecular weight, leading to a much higher boiling point than would be expected from unassociated molecules.

Water also has another unusual property compared to other liquids - a very high heat of evaporation per unit weight. This is shown in Table II (1).

Table II - Heats of Evaporation of Liquids

<u>Substance</u>	<u>Kcal/gm.</u>	<u>Kcal/mole</u>
Water	0.54	9.7
Hexane	0.08	6.9
Carbon tetrachloride	0.05	7.2
Ethyl alcohol	0.20	9.3
Acetone	0.12	6.9
Mercury	0.07	14.1
Bromine	0.04	7.1
Benzene	0.09	7.4

When it comes to firefighting, we can take advantage of these unusual properties of water in two ways. The first (discussed in an earlier publication (2)) is to use water in highly atomized form so that the droplets get sucked into the flame front by the convective currents caused by the fire, and then, by evaporation, absorb so much heat that the flame itself is cooled to below its kindling temperature and it goes out. Fantastically small amounts of water are needed - the trick is to get the droplets into the flame itself, no easy task. The second, which is the thesis of this paper, is to modify the fluidity of water so it can adhere to

vertical and overhead surfaces, and not have most of it run off and be wasted. This can be accomplished by making the water glutinous, either by making a foam (e.g., shaving cream), or giving it a very high viscosity with a thickening agent (e.g., gravy), or both.

Use of Water for Firefighting

The main function of water in conventional firefighting is to cool. We usually do this by dumping excessive amounts of water on the fire. In a Class B (liquid fuel) fire, the water, being denser, sinks under the fuel and thus is wasted. In Class A (solid) fires, water itself is so fluid that it runs off vertical and overhead surfaces, and most of it is wasted.

For Class B pool (two-dimensional) fires, e.g., on the flight deck of aircraft carriers, such as in the disasters on the USS FORRESTAL, ENTERPRISE, NIMITZ, etc., and most commercial airports, proper use of Aqueous Film Forming Foam (AFFF) (developed at NRL in 1964 (3)), can give total control in minutes or even seconds. For propelled or cascading liquids (three dimensional), as happened on the USS RANGER fire when JP-5 jetted out of an open sounding tube in the machinery space, or from cascading fuel from crashed aircraft on USS NIMITZ, agents such as Halons, dry chemicals (PKP - also developed at NRL (4)), carbon dioxide (CO₂), nitrogen (the pressurization concept also developed at NRL (5)), and, eventually maybe even water mist (2) must be used. These are separate problems which will not be discussed further here.

Let us now consider conventional Class A fires. First, let's look at spaces internal to combustible structures (e.g., buildings), such as rooms or compartments. Very roughly (if one thinks of a cube), 5/6 of the exposed surfaces are vertical (walls, bulkheads, sides of furniture, drapes) and overhead (ceiling). Also, these surfaces are most at risk in a fire (recall that fires tend to go up). The floor and horizontal surfaces on furniture, only about 1/6 of the total surface, are much less at risk because they are low and get much less heat, and furthermore, if flat, will often be covered by water (sometimes inches to feet deep). So, in conventional firefighting, we try to wet the vertical and overhead surfaces with a jet of water coming out of a nozzle at up to 100-150 psi (nozzle pressure) and delivering up to 100-200 gal/min, and with a high forward velocity. This is so we can reach (i.e., "throw" the water a distance). But maybe it's also because water is too readily available from the hydrant and pumper. Now, in real fires, we very often have somewhat obstructed surfaces which are not easily wetted because of things in the way, and, on those surfaces we do wet with this massive deluge, most of the water runs off - to say nothing of damage done by breaking and throwing things around with all that momentum energy in the water stream. To be effective in preventing fire spread, we must keep on "hitting" these surfaces over and over again, because what little water stays on the surface quickly evaporates from the heat and can no longer keep the surface cool.

To illustrate this further, let's look at some figures and a simple model on heat transfer. Surfaces exposed to a fairly hot fire receive 2-3 watts/cm², mostly radiant. This is roughly 35 calories/min/cm². Now let's think about this particular square centimeter (cm²) for a moment. Since a calorie is defined as the heat necessary to raise 1 gram of water 1 degree centigrade, this amount of heat would raise the temperature of 1 gram of water from room temperature to roughly its boiling point in ca. 2 min. But if a gram of water, which has a volume of one centimeter cubed, were attached to a square centimeter of vertical surface, it would stick out for a distance of one whole cm, and liquid water just won't stay put in that fashion. It runs off. Suppose, however, our vertical 1 cm² wetted surface can momentarily hold a 0.1 mm layer of water without running off, it's volume would then be 1/100 cm (equivalent to 1/100 gram). It would then take only about 1/50 min. exposure to our model fire to heat it to its boiling point, i.e., roughly 1.2 seconds. Now we start boiling this 1/100 gram of water. From Table II we see that 1/100 of 540 cals (5.4 cals) would be needed to evaporate it. At 35 cal/min./cm², this then would take an additional 1/6 min, or 10 seconds. Thus for a total of 11.2 sec., that 1 cm² surface could not get hotter than the boiling point of water (100°C), and this temperature is way below the pyrolysis temperature of all common building materials. However, the specific heats of such materials are such that they could now heat up more in a hurry and very soon be ready themselves to contribute to the propagation of the fire. For example, we have shown that 3W/cm² will ignite a dry wood crib (Underwriters Laboratories, Type B, 12 x 12 x 12 in.) in 20 seconds (6) and that Ponderosa Pine will start burning at a surface temperature of 265°C (7). It has also been shown that flashover will occur at about 2W/cm² (8).

Now, suppose instead of a 0.1 mm thick layer, we could hold considerably more water on the surface. Think of the protection that would "buy". Here's where glutinous water comes in.

Glutinous Water

As mentioned earlier, water can be made glutinous by foaming, thickening, or both. For a foam to stick to a surface it has to be quite "dry". This means on the order of what is called an expansion ratio of at least 10 or more to one (i.e., 9 parts air, 1 part liquid). Generally, expansion ratios less than ten give foams that are too "soupy" which will run off vertical or overhead surfaces. (Shaving cream foams are considerably higher than 10). If we can make a 10:1 foam stick 1 cm thick on a wall, this is

We took a 30 x 30 cm. piece of raw plywood, wet one side and let it drain a few seconds. We found it gained 9 grams in weight. Although most of this water soaked in, it was equivalent to 0.1 mm thickness of water. A painted surface would "hold" much less.

equivalent to 1 mm thickness of liquid water, or 10 times the amount of our earlier 0.1 mm model. This means it would "buy" 10 times the protection, a very sizeable increase! Even a 1 cm thick layer of 20:1 expansion foam would give 5 times the protection, still worth "buying". Directing water from a fire hose to give a sticky foam can be accomplished using soap (or surfactant), water, compressed air, the ratios being easily controlled to suit the occasion. [N.B. For a point of reference, the better aerating nozzles used to make AFFF foam by aspirating air, give a foam with an expansion ratio of ca. 6:1 which is too "thin" to stick).

Thickening of water is another way of making it glutinous. For firefighting purposes, an additive that gives a higher viscosity (e.g., starch, methyl cellulose, polymers, etc.), or even use of a thixotropic material (e.g., clay) would probably be more desirable than a gel type with internal molecular structure (e.g., jello), because we want it to stick rather than slither off. Many materials can be used as "thickeners" and/or thixotropes, and their choice would depend on the usual criteria of availability (cost), ease of application, performance, toxicity, environmental impact and even cleanability (after the fire).

One advantage of a thickened glutinous water over the foamed types is that more water can be made to stick to the surface, up to the equivalent of several millimeters thick. In our earlier models we used an example of foam that ostensibly gave us 5 - 10 times the time of protection. If we could get a thickened layer equivalent to water 5 mm deep, then in our model our protection should be quintupled again, or 50 times that of plain water. In the real world this is probably optimistic (the model is too simplistic), but the concept is there, and we should be able to get manyfold protection regardless.

To illustrate this "added" protection we ran a simple experiment a number of years ago on protection of overhead surfaces in a fire situation (9). It consisted of cutting ordinary 1/4" plywood into 1 x 4 ft. panels and then "coating" one of each with: (a) plain water (i.e., wet with a hose); (b) AFFF foam (6%) (from a 2 - 1/2 gal. extinguisher); (c) a proprietary glutinous material called Fire Lock 5000 (from a 2 1/2 gal extinguisher); and (d) a similar material called Fire Lock ABD. We suspended these plus a dry panel (control) horizontally about 3 ft over a JP-5 (jet fuel) pit fire, with the coated surfaces down. The panels were placed on two cross strips of angle iron about 6" from their ends. Table III gives the times when surface ignition was readily evident, and when the panels burned to "failure" by collapsing into the fire off the two angle iron tracks originally holding them in place.

It took about 15 sec for the pit fire to become fully involved (i.e., for the flames to impinge on the panels), so some number such as this should be subtracted from the times listed to give a more realistic comparison of the impact of the "coatings". Also, in the case of the two glutinous water panels, both the basic mix

and their method of application were a long cry from being optimized, and the thickness of the coating was very irregular, which probably explains why "time to ignition" seems short - the really thin spots dried up and allowed small batches of the wood substrate to start burning, but the thicker areas protected the whole panels from collapsing. Also, the consistency of the Fire Lock 5000 was on the "runny" side and much of it sloughed off when the panels were mounted.

Table III
Resistance of "Coated" Plywood Panels to A JP-5 Fire
(In min:sec from time of ignition of the pit)

<u>Panel</u>	<u>Time to Ignition*</u>	<u>Time to Failure</u>
Blank (dry)	0:36	2:35
Plain Water	0:44	2:44
AFFF (6%)	1:01	3:27
Glutinous Water (Fire Lock 5000)	1:50	4:24
Glutinous Water (Fire Lock ABD)	1:30	10:04

* - These numbers are very imprecise because it was very difficult to distinguish flames from the panels from the overlapping flames from the pit.

The results of this simple experiment vividly demonstrate the effectiveness of glutinous water, not only in protecting a combustible from fire, but also in the economy of water. Thus, after 2 min. 35 sec., the blank panel was already in the pit contributing to the fire and exacerbating it, whereas the better glutinous panel was still resisting fire at 10 min. Furthermore, in the plain water panel, practically all the water ran off during application (and was wasted), whereas in the better glutinous panel most of what was applied stuck to the panel. This in itself would be very important in places where water is at an extreme premium such as certain warfare theaters of operation, forest fires, remote areas, etc. It also brings up the element of time in conventional firefighting in that if a firefighter "coats" a surface with glutinous water, he/she doesn't have to come back and keep reapplying it like he/she does with water. He/she can be much more effective and efficient by being able to move on to fight other parts of the fire. And, in the overall scheme of things, the "protected" surface is not going to be contributing to potential fire growth behind their backs the way it might were plain water used.

Now, let's take our model one step further. Let's design our system so we can dispense a foaming agent, or a thickener, or both depending on what's needed. This could easily be accomplished at a firefighting pumper with an air compressor and an injector (or eductor). The advantage of using both foam and thickener ("superglutinous" water) is that more actual water can be made to stick to vertical and overhead surfaces thus giving even greater protection (both time and fire spread) and greater economy of water. One could even get fancy (it is tempting to get carried away) and suggest incorporation of a very high albedo powder (little mirrors) into the "soup" so as to reflect the infra-red radiation and thus "buy" even greater protection. Or, incorporate a dry chemical or other firefighting agent. However, in the real world, such concepts could only offer merit in extreme situations, such as protection of flammables in desert warfare.

EPILOGUE

It is not the thesis of this paper to tell how glutinous water should be prepared or how best to use it. Suffice it to say that though this concept is not new, nevertheless the author believes that its advantages are sufficiently great that we (as a firefighting community) should be addressing it much more vigorously. The author leaves to others such things as the best ways to put an air compressor on a pumper, and what pressures and flows to use, and what kinds of materials are best for foaming and/or thickening water. The author is well aware that the scientific literature describes a myriad of substances such as polymers, swelling agents, particulates, etc., both natural and synthetic, that could be used. The author is also very strongly of the belief that anything we can do to "buy time" (the subject of another paper (10)), such as by the use of glutinous water, is worth looking into and using.

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